


PATENT COOPERATION TREATY

PCT

INTERNATIONAL PRELIMINARY REPORT ON PATENTABILITY (Chapter II of the Patent Cooperation Treaty)

(PCT Article 36 and Rule 70)

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| Applicant's or agent's file reference PA134799/PCT | | FOR FURTHER ACTION | | See Form PCT/PEA/416 |
| International application No. PCT/IB2004/000656 | | International filing date (day/month/year) 10.03.2004 | | Priority date (day/month/year) 10.03.2003 |
| International Patent Classification (IPC) or national classification and IPC C07C7/10, C10G21/16 | | | | |
| Applicant SASOL TECHNOLOGY (PROPRIETAY) LIMITED | | | | |
| <p>1. This report is the international preliminary examination report, established by this International Preliminary Examining Authority under Article 35 and transmitted to the applicant according to Article 36.</p> <p>2. This REPORT consists of a total of 5 sheets, including this cover sheet.</p> <p>3. This report is also accompanied by ANNEXES, comprising:</p> <p>a. <input checked="" type="checkbox"/> sent to the applicant and to the International Bureau) a total of 3 sheets, as follows:</p> <p><input checked="" type="checkbox"/> sheets of the description, claims and/or drawings which have been amended and are the basis of this report and/or sheets containing rectifications authorized by this Authority (see Rule 70.16 and Section 607 of the Administrative Instructions).</p> <p><input type="checkbox"/> sheets which supersede earlier sheets, but which this Authority considers contain an amendment that goes beyond the disclosure in the international application as filed, as indicated in item 4 of Box No. I and the Supplemental Box.</p> <p>b. <input type="checkbox"/> (sent to the International Bureau only) a total of (Indicate type and number of electronic carrier(s)) , containing a sequence listing and/or tables related thereto, in computer readable form only, as indicated in the Supplemental Box Relating to Sequence Listing (see Section 802 of the Administrative Instructions).</p> | | | | |
| <p>4. This report contains indications relating to the following items:</p> <p><input checked="" type="checkbox"/> Box No. I Basis of the opinion</p> <p><input type="checkbox"/> Box No. II Priority</p> <p><input type="checkbox"/> Box No. III Non-establishment of opinion with regard to novelty, inventive step and industrial applicability</p> <p><input type="checkbox"/> Box No. IV Lack of unity of invention</p> <p><input checked="" type="checkbox"/> Box No. V Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement</p> <p><input type="checkbox"/> Box No. VI Certain documents cited</p> <p><input type="checkbox"/> Box No. VII Certain defects in the international application</p> <p><input type="checkbox"/> Box No. VIII Certain observations on the international application</p> | | | | |
| Date of submission of the demand 06.01.2005 | | Date of completion of this report 13.06.2005 | | |
| Name and mailing address of the international preliminary examining authority:  European Patent Office - P.B. 5818 Patentlaan 2 NL-2280 HV Rijswijk - Pays Bas Tel. +31 70 340 - 2040 Tx: 31 651 epo nl Fax: +31 70 340 - 3016 | | Authorized Officer O'Sullivan, P Telephone No. +31 70 340-4511 | | |



**INTERNATIONAL PRELIMINARY REPORT
ON PATENTABILITY**

International application No.
PCT/IB2004/000656

Box No. I Basis of the report

1. With regard to the **language**, this report is based on the international application in the language in which it was filed, unless otherwise indicated under this item.

☐ This report is based on translations from the original language into the following language , which is the language of a translation furnished for the purposes of:

- ☐ international search (under Rules 12.3 and 23.1(b))
☐ publication of the international application (under Rule 12.4)
☐ international preliminary examination (under Rules 55.2 and/or 55.3)

2. With regard to the **elements*** of the international application, this report is based on *(replacement sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to this report):*

Description, Pages

1, 2, 4-13 as originally filed
3 received on 10.05.2005 with letter of 10.05.2005

Claims, Numbers

1-14 received on 10.05.2005 with letter of 10.05.2005

Drawings, Figures

1-3 as originally filed

☐ a sequence listing and/or any related table(s) - see Supplemental Box Relating to Sequence Listing

3. ☐ The amendments have resulted in the cancellation of:

- ☐ the description, pages
☐ the claims, Nos.
☐ the drawings, sheets/figs
☐ the sequence listing (*specify*):
☐ any table(s) related to sequence listing (*specify*):

4. ☐ This report has been established as if (some of) the amendments annexed to this report and listed below had not been made, since they have been considered to go beyond the disclosure as filed, as indicated in the Supplemental Box (Rule 70.2(c)).

- ☐ the description, pages
☐ the claims, Nos.
☐ the drawings, sheets/figs
☐ the sequence listing (*specify*):
☐ any table(s) related to sequence listing (*specify*):

* If item 4 applies, some or all of these sheets may be marked "superseded."

**INTERNATIONAL PRELIMINARY REPORT
ON PATENTABILITY**

International application No.
PCT/IB2004/000656

Box No. V Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

1. Statement

| | | |
|-------------------------------|-------------|------|
| Novelty (N) | Yes: Claims | 1-14 |
| | No: Claims | |
| Inventive step (IS) | Yes: Claims | 1-14 |
| | No: Claims | |
| Industrial applicability (IA) | Yes: Claims | 1-14 |
| | No: Claims | |

2. Citations and explanations (Rule 70.7):

see separate sheet

Re Item V

**Reasoned statement with regard to novelty, inventive step or industrial applicability;
citations and explanations supporting such statement**

Reference is made to the following documents:

- D1: WO 02/31085 A
- D2: US-A-4 603 225
- D3: DE 199 11 910 A
- D4: US-A-4 686 317

1. Novelty (Art 33(2) PCT)

1.1 D1 discloses a process for separating olefins and paraffins from oxygenates in a liquid hydrocarbon stream (see page 3, paragraph 1- page 4, paragraph 4). The hydrocarbon, which originates from a Fischer-Tropsch process, is first distilled to give, for example, a C₄ to C₁₈ hydrocarbon. The oxygenates are separated therefrom by extraction with a polar solvent which comprises a mixture of water and an organic liquid such as, but not limited to, propanol. The water typically comprises no more than the azeotropic composition of water in the organic liquid. There is no mention of methanol as polar solvent, Present claims 1-14 can therefore be considered novel over D1.

1.2 D2 discloses (claim 1 and 5) a process for separating dimethyl ether from a hydrocarbon mixture which comprises contacting said hydrocarbon mixture with an aqueous solution containing a polar oxygenated hydrocarbon, preferably methanol. D2 however does not disclose a hydrocarbon stream in the C₈₋₁₆ range, nor that an extract from the liquid-liquid extraction is sent to a solvent recovery column. Present claims 1-14 can therefore be considered novel over D2.

1.3 D3 (column 1, lines 1-25) discloses the liquid-liquid extraction of oxygenates from a C₈ hydrocarbon stream. The solvent chosen is a solution of either methanol, ethanol, propanol or butanol in water. D3 however does not disclose a hydrocarbon stream in the C₈₋₁₆ range. Present claims 1-14 can therefore be considered novel over D3.

1.4 D4 discloses a process for removing oxygenated impurities from Fischer-Tropsch

naphtha (and its subsequent oligomerization to produce liquid hydrocarbon fuels. The oxygenates are removed by liquid-liquid extraction using a polar organic solvent, containing a 2-aminoalkanol. Table 2 lists however solvent systems for which the extraction has been tested and the final solvent is 25% MeOH in H₂O. However, D4 also discloses (column 3, lines 8-13) that the solvents used for extracting the oxygenates are heavy boiling relative to the oxygenated compounds contained in and removed from the hydrocarbon stream. The solvent is therefore recovered as a bottoms product in the solvent recovery column (rather than a tops products as in present claim 1). Present claims 1-14 can therefore be considered novel over D4.

2. Inventive Step (Art 33(3) PCT

The present subject-matter is considered novel over the prior art documents D1-D4. Additionally there appears to be no suggestion nor teaching within these documents which could be prejudicial to the acknowledgement of inventive step for present claim 1. Present claims 1-14 may therefore be considered inventive.

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SUMMARY OF THE INVENTION

According to the invention, there is provided a commercially viable process for extracting oxygenates from a hydrocarbon stream containing a range of hydrocarbons in the C_6 to C_{16} range, typically a fraction of the condensation product of a Fischer-Tropsch reaction, while preserving the olefin content of the condensation product.

The oxygenate extraction process is a liquid-liquid extraction process that preferably takes place in an extraction column using a mixture of methanol and water as the solvent, wherein an extract from the liquid-liquid extraction is sent to a solvent recovery column from which a tops product comprising methanol, olefins and paraffins is recycled to the extraction column, thereby enhancing the overall recovery of olefins and paraffins. A bottoms product from the solvent recovery column may also be recycled to the extraction column.

The solvent preferably has a water content of more than 3% by weight, more preferably a water content of from 5% - 15% by weight.

Preferably, a raffinate from the extraction column is sent to a stripper column from which a hydrocarbon feed stream containing more than 90% by weight olefins and paraffins and typically less than 0.2% by weight, preferably less than 0.02% by weight oxygenates exits as a bottoms product. The recovery of olefins and paraffins over the oxygenate extraction process is preferably greater than 70% more preferably greater than 80%, while the olefin/paraffin ratio is at least substantially preserved.

According to another aspect of the invention, the solvent recovery column includes an extract inlet, an upper overhead outlet and a lower bottoms outlet, with a side-draw located above the extract feed point and below the overheads outlet.

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CLAIMS

1. A process for extracting oxygenates from a hydrocarbon stream containing a range of hydrocarbons in the C₈ to C₁₆ range, the process including the step of extracting the oxygenates in a liquid-liquid extraction process using a mixture of methanol and water as the solvent,

wherein an extract from the liquid-liquid extraction is sent to a solvent recovery column from which a tops product comprising methanol, olefins and paraffins is recycled to the extraction step, thereby enhancing the overall recovery of olefins and paraffins.

2. The process according to claim 1, wherein the aqueous phase of a bottoms product from the solvent recovery column is recycled to the extraction step.
3. The process according to any one of the preceding claims, wherein the extraction step takes place in an extraction column.
4. The process according to any one of the preceding claims, wherein the solvent introduced to the extraction step has a water content of more than 3% by weight.
5. The process according to claim 4, wherein the solvent has a water content of from 5% - 15% by weight.
6. The process according to any one of the preceding claims, wherein the olefin/paraffin ratio of the hydrocarbon stream is substantially preserved after the extraction step.
7. The process according to any one of claims 3 - 6, wherein a raffinate from the extraction column is sent to a stripper column from which a hydrocarbon feed stream containing more than 90% by

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weight olefins and paraffins and less than 0.2% by weight oxygenates exits as a bottoms product.

8. The process according to claim 7, wherein the bottoms product contains less than 0.02% by weight oxygenates.
9. The process according to any one of the preceding claims wherein the recovery of olefins and paraffins over the oxygenate extraction step is greater than 70%.
10. The process according to claim 9, wherein the recovery of olefins and paraffins over the oxygenate extraction step is greater than 80%.
11. The process according to any one of claims 1 – 10, wherein the solvent recovery column includes an extract inlet, an upper overhead outlet and a lower bottoms outlet, with a side-draw located above the extract feed point and below the overheads outlet.
12. The process according to any one of the preceding claims wherein the hydrocarbon stream is the fractionated condensate product from a low temperature Fischer-Tropsch reaction.
13. The process according to any one of the preceding claims wherein the hydrocarbon stream contains 5 – 15% by weight oxygenates.
14. The process according to any one of the preceding claims wherein the fractionated hydrocarbon condensate product is in the C₁₀ to C₁₃ range.